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HYDRONIUM ZIRPSIOS: FIELD ASSISTED ION EXCHANGE OF Na-ZIRPSIOS

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March 1983

Project ERP-4.5.0.2.03
Hydrogen-Air Fuel Cell

23pp

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 83-47 (IR)

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by

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ABSTRACT

A study of the exchange of the sodium ions by hydronium ions in Na-zirpsios by an electrical field assisted process is described. The ion exchange takes place quite readily, but during the process the product tends to develop cracks, either due to the presence of grain boundary impurities such as glass or due to the severity of the lattice expansion during the substitution of sodium ions by the considerably larger hydronium ions.

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CONTENTS

	Page
Abstract	1
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	3
Materials for Exchange	4
Characterization of the Exchange Products	4
RESULTS AND DISCUSSION	5
Current-Voltage Characteristics of Na-zirpsio	5
Voltage Characteristics of the Cell during Exchange at Constant Current	5
The Exchange Behaviour of Na-zirpsios	5
Microscopic Examination of the Products	6
SEM Studies	6
X-ray Diffraction Analysis	7
Microhardness Measurements	7
CONCLUSIONS	8
ACKNOWLEDGEMENTS	9
REFERENCES	10

TABLES

1.	Summary of data on hydronium ion exchange runs	11
2.	Microhardness of zirpsios before and after exchange	12

FIGURES

1.	A schematic diagram of the experimental set-up for Na^+ to H_3O^+ ion exchange	13
2.	A photograph of an assembled exchange cell	14
3.	Voltage versus current characteristics of Na-zirpsio	14
4.	The change in field voltage during exchange at constant current	15
5.	Transmitted light photographs of zirpsio disc before and after exchange	15

Page

6. Photograph showing extensive cracking on ion exchange 16
7. Low magnification images of a partially exchanged zirpsio sample:
   (a) SEM
   (b) Energy dispersive X-ray map of Na (K_α) .....
8. SEM of a cracked zone in Na-zirpsio after hydronium ion exchange 16
9. Guinier X-ray diffraction pattern of Max Planck x = 1.5 Na-zirpsio and hydronium zirpsio 18
10. Guinier X-ray diffraction pattern of Hong x = 2.1 Na-zirpsio and hydronium zirpsio 19

INTRODUCTION

The development of practical devices that exploit the unique properties of a variety of solid electrolytes stems from the pioneering work of Kiukkola and Wagner in 1957 (1) who used doped zirconia electrolytes to determine the free energy of formation of various oxides using an electrochemical cell. That work stimulated R&D in both cationic- and anionic-conducting materials so that by the mid 1960's, extensive work was underway to develop a number of silver- and sodium-conducting electrolytes and employ them in various devices such as coulometers, strain gauges, microbatteries (Ag) and high energy density batteries (Na).

The development of batteries based on sodium-conducting electrolytes, which was pioneered by the Ford Motor Company in 1967, stimulated an extensive amount of fundamental research in all the developed nations into the production, characterization and utilization of the basic electrolyte material known as beta"-alumina (nominally having a composition of $Na_2O:Al_2O_3$ in the range between ≈1:4.5 and 1:7.5). From that work, it was soon realized that a wide range of electrolytes could be produced based on the beta-alumina structure in which not only Group I cations but also Group II cations of the Periodic Table were mobile.

During the early 1970's, the interest in this class of materials was given an added stimulus by the decision of the OPEC nations to drastically increase the cost of crude oil. Intensive and extensive research was started in various parts of the world for developing alternative energy sources and for their efficient use. Because of their projected high efficiency and other advantages, hydrogen fuel cells were considered to play an important part in the energy field of the future. The most convenient and efficient use of hydrogen in hydrogen-air fuel cells requires the development of reliable hydrogen ion conducting solid electrolytes. Hydronium (or oxonium) beta alumina has been known since 1968 (2) and it was realized that this material could be of value in the development of a hydrogen-based fuel cell. Consequently, a number of materials research groups started an investigation of this and other potential hydrogen-conducting electrolytes and gradually a series of principles that controlled the formation and behaviour of this new group of materials were discovered.

Extensive examination of the original hydrogen-conducting beta-alumina using nuclear magnetic resonance (NMR) suggested that the conductivity was due to the hopping of a H^+ ion from one lattice H_2O to another as the hydronium-ion (H_3O^+) and an adjacent water molecule moving into favourable orientations so that the energy barrier between the two is minimized and the proton can move on. Other data showed that this particular material was only stable up to about 520 K, above which it suffers a partial dehydration and drastic loss of conductivity; above about 720 K the material is completely dehydrated and collapses to gamma-alumina.

Clearly, such material, which must be impermeable and have a reasonable strength [10,000 psi (69 MPa)] in the hydronium form, can only be produced indirectly by the ion exchange of a sintered, high-density, high-strength precursor material. Initially, it was thought necessary to produce a precursor material in which the ionic radius of the ion to be displaced was of similar size to that of the hydronium ion (≈ 1.50 Å). Consequently, the earlier work at the Ford Motor Company focussed on the development of a potassium-containing beta-alumina (ionic radius of K: 1.33 Å). Because of their difficulty in ion-exchanging a Na beta"-alumina to the K form at room temperature without shattering the material due to the insertion of an ion nearly 40% larger into the lattice sites occupied initially by the sodium (Na: 0.97 Å), the Ford researchers used a vapour-phase ion exchange process in which a sodium beta"-alumina was heated in potassium vapour at 1673 K for an extended period. Under these conditions, the strain induced in the lattice is annealed at the high temperature and a potassium beta-alumina is produced (3).

More recently, the suggestion that the process to produce a hydrogen conductor must involve the ion exchange of ions of similar size has been questioned by researchers at the Max Planck Institute, Stuttgart, who claimed that a hydrogen-conducting electrolyte can be produced by the slow ion exchange of a sodium conductor directly to a hydrogen conductor without the need to go through the intermediate potassium form. Their technique is based on the exchange of the material in a weakly acidic solution using a dc polarizing voltage as an additional driving force to displace the sodium and gradually introduce the H_3O^+ ions. In this manner, they have been able to ion exchange one of the three-diminsional sodium-conducting electrolytes known as Na-zirpsio to a hydrogen-conducting form.

The practical implications of this claim are considerable, for if it proves to be that a sodium conductor can be readily (if slowly) converted to a hydrogen-conducting form, thereby avoiding the need to produce an intermediate potassium form, the route to the production of hydrogen-conducting electrolytes will be greatly simplified. Consequently, because the CANMET program has been examining the production and characteristics of a number of electrolytes including the beta-aluminas and the Na-zirpsios, the use of this field assisted technique in ion exchanging a number of different compositions of Na-zirpsios has been recently studied. The present report details the conditions under which the materials were exchanged and a preliminary examination of the products obtained.

EXPERIMENTAL PROCEDURE

A modified version of the procedure outlined by Bell and Hofer (4) was used in the present investigation for the field assisted ion exchange of various Na-zirpsio samples. A schematic diagram of the experimental set-up is shown in Fig. 1. An exchange cell, C, was constructed by sealing a 1.27 cm diameter Na-zirpsio disc onto a hole drilled at the bottom of a plastic vial, 3.5 cm in diameter by about 6 cm in height, using silicone rubber cement. A photograph of an assembled cell is given in Fig. 2.

After curing of the cement, the cell was filled with 0.1 N sulphuric acid and placed in a beaker of 0.1 N sulphuric acid. Two platinum foil electrodes - one inside the cell and the other in the outer bath - were introduced into the acid on both sides of the specimen to be exchanged. The outer and inner electrodes were respectively connected to the positive and negative terminals of a constant current dc power supply (Hewlett - Packard 120 V-120 mA) through an ammeter. A voltmeter was connected between the two cell electrodes in order to measure the field voltage. The power supply could be worked either in a constant current or in a maximum voltage limited mode. On switching the current on, the only passage for the electricity is through the sample to be hydrogen-exchanged. Consequently, the hydronium ions that are moving from the positive electrode to the negative electrode in the electrolytic system try to pass through the sodium ion conducting material and in the process replace the sodium ions with hydronium ions. The current on the positive side of the cell is carried by the hydronium ions and that on the negative side by

sodium ions until the exchange is complete. The process, thus, is very simple and the control of the energy of the hydronium ions displacing the sodium ions is also easy by controlling the current density through the specimen.

The sodium ions generated in the negative compartment react with the water in the chamber forming hydrogen ions, which are discharged to form hydrogen gas at the negative electrode, and alkali in solution. This causes the pH inside the cell to increase until the progress of the ion exchange is complete. The pH of the solution inside the cell is kept below 7.0 by the intermittent addition of 0.1 N sulphuric acid in order to prevent any decomposition of the product by reaction with alkali. At the positive electrode oxygen is evolved.

In the field assisted hydronium ion exchange process, thus, a hydronium ion front proceeds through the sodium ion conducting solid and the velocity of this front-movement depends on the voltage of the field. However, it is important to make sure that the voltage used for the exchange is not high enough to cause the decomposition of the ceramic concerned.

Materials for Exchange

Two types of Na-zirpsios, sintered Hong (5) and Max Planck (6) compositions, with x = 1.5, 1.8, 1.9, 2.0 and 2.1, were used for the exchange studies. A sample of hot-pressed Na-zirpsio (Hong, x = 2.0) was also examined. The Na-zirpsio precursor powders were prepared by the standard gel processing technique developed at CANMET (7). The procedure for the synthesis and sintering of the various materials is described elsewhere (8). Most of the materials had high relative densities and fine microstructure.

Characterization of the Exchange Products

After the exchange process, the discs were characterized generally by their dimensional changes (when possible), X-ray diffraction analysis, microscopy (both light and scanning electron), microprobe and microhardness tests. These studies provided an insight into the changes taking place within the material during the ion exchange process.

Faraday's laws apply to the field assisted ion exchange of the Na-zirpsios because it is an electrolytic process. Hence the amount of electricity required to exchange the mobile sodium ions in the Na-zirpsio

can be calculated knowing that one gram-ion of sodium is liberated by 96500 coulombs, and one ampere per second represents one coulomb of electricity.

RESULTS AND DISCUSSION

Current-Voltage (i-v) Characteristics of Na-zirpsio

Fig. 3 shows the nature of the variation of current passing through the Na-zirpsio disc with a change in the applied voltage to the exchange cell. The inflexion point at about 25 V represents the break-down potential of the cell. The exchange experiments were carried out using a variety of voltage and current conditions both above and below 25 V. Because a current density of about 50 mA per cm^2 is required for a practical fuel cell, initial experiments were performed at similar current densities.

Voltage Characteristics of the Cell during Exchange at Constant Current

A typical plot of the change of voltage with time during the hydronium ion exchange in a Na-zirpsio sample at constant current is presented in Fig. 4. The voltage decreases consistently with time until it reaches a constant value. This is contrary to the expected behaviour because hydronium zirpsio is reported to be a poorer conductor than Na-zirpsio (4). The reason for the decrease of cell voltage with increased exchange may be the formation of small leakage paths in the Na-zirpsio through the development of microcracks.

The Exchange Behaviour of Na-zirpsios

A list of the various samples subjected to field assisted hydronium ion exchange, the conditions under which they were exchanged and the visually observed condition of the discs after exchange are displayed in Table 1. All the specimens developed cracks to varying degrees depending essentially on the current density (or field voltage) that was employed for the exchange. The samples that were ion exchanged at high current densities invariably broke down drastically and on removal of these specimens from the cell they disintegrated into many pieces. Only the specimens that were exchanged at the lowest power levels showed any sign of integrity and even these could be easily broken by hand by a gentle bending force. An expansion of 2-3% was observed in the physical dimensions of the disks.

Microscopic Examination of the Products

Transmitted light photographs of a disc before and after exchange are shown in Fig. 5. Before exchange the sample is clear, (a); but after exchange, although the sample appears to stay together, it is full of internal cracks (b). A photograph of another sample that underwent serious cracking on exchange is shown in Fig. 6. The entire sample is covered with straight and jagged cracks.

SEM Studies

Polished sections of the exchanged discs were prepared and were examined in the scanning electron microscope. A low magnification image of a partially ion exchanged sample of Na-zirpsio is shown in Fig. 7a. Fig. 7b is a sodium K-alpha energy dispersive X-ray map of the same field. The boundary between the exchanged and original material is clearly visible in these photographs. The sodium concentration in the unexchanged zone is still high whereas that in the exchanged zone is very low. The exchanged areas are full of cracks, pores and pull-outs; in the unexchanged areas these defects are considerably less numerous.

Fig. 8 is a scanning electron micrograph of a field of hydronium zirpsio through which a crack has been developed. It has a river-like appearance with numerous tributaries joining in. These cracks are definitely not representative of sub-lattice defects as may be expected from a lattice expansion stand-point. They appear more like grain boudary cracks, mostly propagating through the grain boundary phases. This phenomenon suggests that the cracking of the Na-zirpsio disc on hydronium exchange may be caused mainly by the highly reactive nature of the grain boundary phases, such as glass, in the sintered Na-zirpsio. The evidence, if any, for the presence of sub-lattice cracks in the product will be impossible to find by using the SEM because such cracks will be too fine to be detected by SEM. The existence of such cracks, hence, is uncertain. Transmission electron microscopic studies might reveal microcracks on such a level.

A microprobe analysis of the total field described above showed that the sodium has been almost completely removed from the material irrespective of the location - whether it is close to the crack or away from the crack. The exchange of sodium ions by hydronium ions, therefore, did take place within the crystal lattice by the experimental technique used.

X-ray Diffraction Analysis

XRD patterns before and after the hydronium ion exchange were obtained either by the Guinier or by the diffractometer technique on several of the samples. The Guinier diffraction patterns for the Max Planck x = 1.5 composition are shown in Fig. 9. It is interesting that the zirpsio still retains the original crystal structure after the ion exchange. The pattern after exchange is, however, different from the original in that some of the peaks have become broad and displaced. The displacement of the peaks is towards larger d-spacing and this demonstrates the expansion of the crystal lattice by the replacement of the smaller sodium ion by the considerably larger hydronium ion.

The change in the XRD pattern of the Hong x = 2.1 sample after exchange is shown in Fig. 10. In this instance, the change in crystal structure is much more pronounced than in the Max Planck x = 1.5 material. The reason for this behaviour is not clear; it may be related to the crystal structure of the product. At x = 1.5, the crystal structure of the Na-zirpsio is rhombohedral and at x = 2.1 it is monoclinic. It is plausible that the monoclinic structure is more drastically affected by the ion exchange than the rhombohedral form.

All the sodium in the Na-zirpsio is not readily available for hydronium ion exchange. Only the mobile sodium ions, which are responsible for the solid state ionic conduction, are easily susceptible to hydronium ion exchange. The number of mobile sodium ions in turn are related to the crystal lattice, which is a function of the composition of the Na-zirpsio solid solution (9). In the present study the progress of the ion exchange was monitored by the change in pH in the negative compartment of the cell and in most cases the exchange was carried out to completion.

Microhardness Measurements

A Tukon micro-macro hardness tester was utilized to measure the hardness of the various Na-zirpsios and their hydronium derivatives. Polished sections of these various materials were used for these measurements. A load of 1.0 kg was applied on a Vicker's indentor for each hardness measurement. Under this applied load the samples produced small cracks at the four corners of the square indentation and the measured hardness was then independent of the applied load. The indentations were made only in areas free of cracks visible under the microscope. Three to

five measurements were made on each specimen. The results are presented in Table 2. It is obvious that the hardness of the hydronium ion exchanged zirpsios drops to a low value of about 3 MPa irrespective of the hardness of the initial Na-zirpsio, which is in the range of 5-9 MPa.

The reason for the drastic decrease of hardness after the exchange of sodium ions by hydronium ions must be either due to the expansion of the crystal lattice, which gives rise to an increase in bond-length and a consequent decrease in packing density, or due to the development of microcracks within the material during the ion exchange, or both. There is evidence for both occurring - XRD data for lattice expansion and microscopic data for crack formation. However, this does not have to be a detriment to the utilization of hydronium zirpsios in hydrogen fuel cells and other devices if they can be made in a macrocrack-free form: the toughness of the material is more important than the hardness, and quite possibly the fracture toughness of the material could increase with a decrease of hardness, especially if microcracks are present. However, if the microcracks cause the leakage of hydrogen gas through the material, it will be detrimental. Further work is indicated for the generation of such information.

CONCLUSIONS

Na-zirpsios can be converted to hydrogen ion conducting solid electrolytes by field assisted hydronium ion exchange in an acid medium. However, in the exchange process the specimens undergo a type of grain boundary cracking and the severity of this cracking is related to the current density used for the exchange. Even at very low current densities, microcracks are produced in the material, which may or may not be detrimental to its application in hydrogen fuel cells and other hydrogen ion conducting devices depending on the hydrogen gas leakage characteristics of the material. These latter characteristics have to be determined.

Hardness measurements using Vicker's indentation method show a drastic decrease in the microhardness of zirpsio when the sodium ions are exchanged by hydronium ions. This is expected, based on the lattice expansion that is occurring during the exchange and also based on the formation of microcracks during ion exchange.

It is suspected that the grain boundary glass phases present in the Na-zirpsios are a major cause of their deterioration during the ion exchange because they tend to form macrocracks in the resulting hydronium zirpsios. The key to the success of the synthesis of hydronium zirpsios by the direct exchange of Na ions from Na-zirpsios appears to lie in the fabrication of glass-free Na-zirpsios.

ACKNOWLEDGEMENTS

The authors are grateful to A.J. Hanson and A.G. McDonald for the assistance in some of the experimental work.

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Table 1 - Summary of data on hydronium ion exchange runs

Sample*	Exchange Conditions			Result**
	Current (mA)	Voltage (V)	Time (h)	
MP x=1.5				
	50	6-25	48.0	cracks
	13	6-25	53.0	small cracks
	13	5-15	5.5	no cracks
	10	4-10	48.0	small cracks
MP x=1.8				
	50	12-52	48.0	cracks
	20	2-6	26.0	cracks
	15	5-28	72.0	small cracks
	15	6-25	56.0	small cracks
H x=1.8				
	80	18-25	56.0	cracks
	40	12-28	24.0	cracks
H x=1.9				
	80	30-68	6.0	cracks
	40	19-38	27.0	cracks
	20	18-26	55.0	cracks
	0	0	48.0	no cracks
H x=2.0				
	100	36-64	170.0	breaks
	60	19-38	6.0	cracks
	40	19-38	50.0	cracks
MP x=2.0				
	8	4-10	22.0	no cracks
H x=2.1				
	100	12-19	120.0	breaks
	20	8-54	51.0	cracks
	20	10-122	25.0	cracks
	5	2-57	216.0	no cracks
MP x=2.1				
	50	10-13	48.0	cracks

*H = Hong, MP = Max Planck composition
**Visual observation

Table 2 - Microhardness of zirpsios before and after exchange;
Indentor: Vicker's; Applied Load: 1.0 kg

Sample		Microhardness, MPa	
		Before exchange	After exchange
Max Planck	x=1.5	9.10	3.37
Max Planck	x=1.8	6.86	3.06
Hong	x=1.9	8.65	3.05
Hong	x=2.0	8.20	2.98

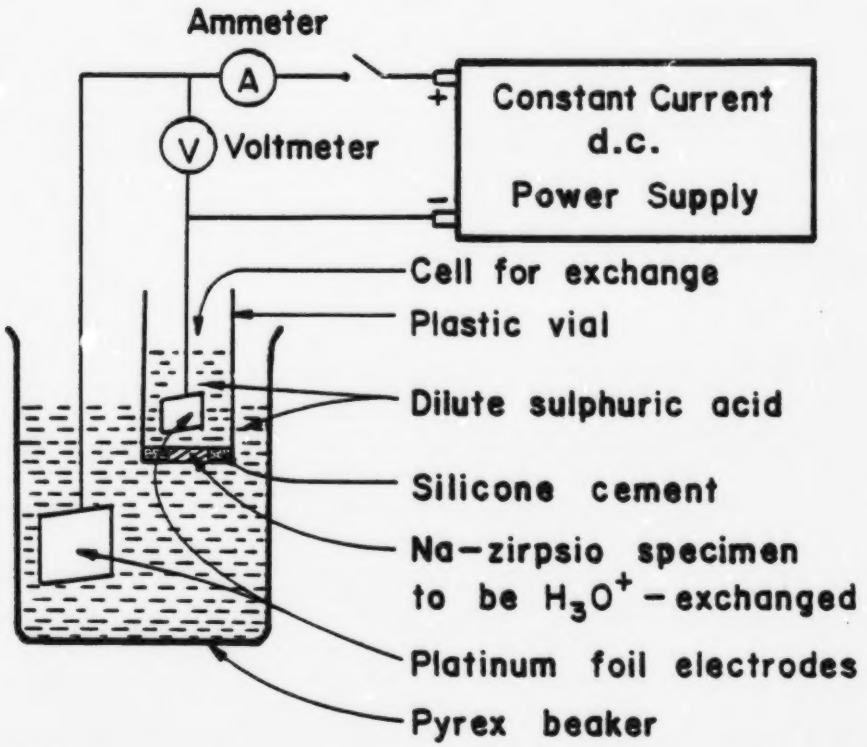

Fig. 1 - A schematic diagram of the experimental set-up for Na^+ to H_3O^+ ion exchange

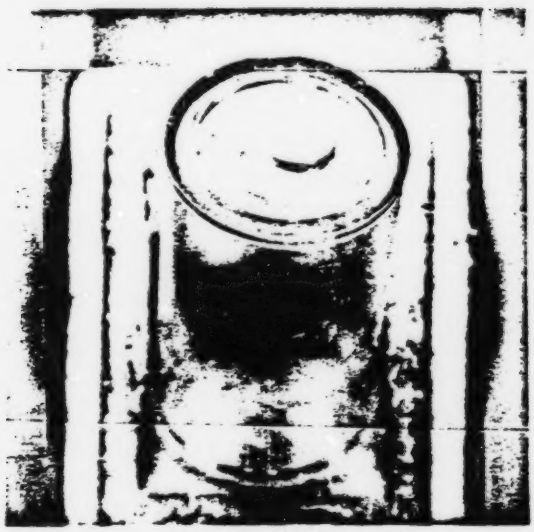

Fig. 2 - A photograph of an assembled exchange cell

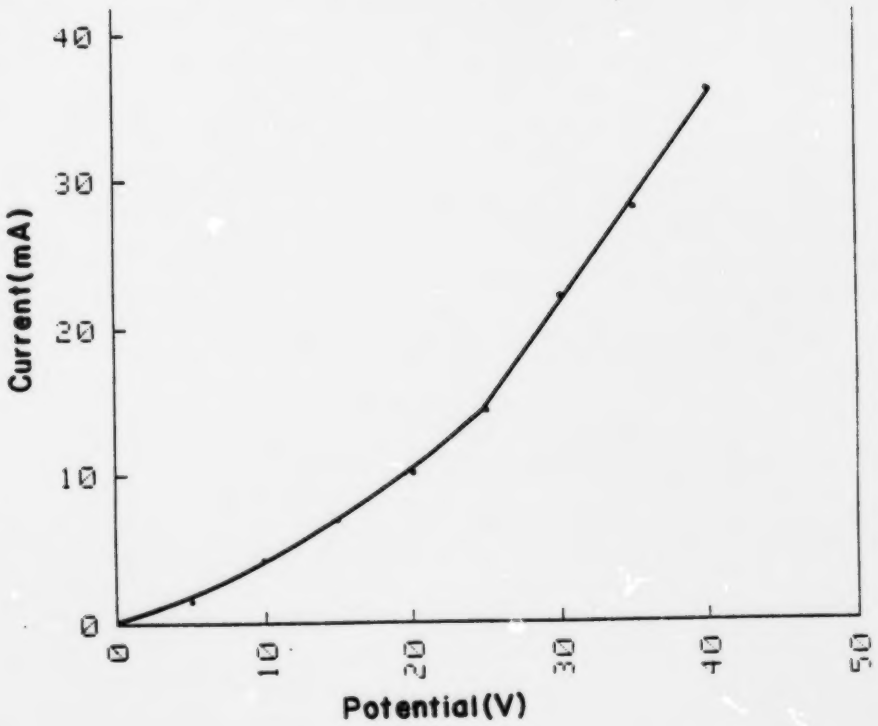

Fig. 3 - Voltage vs. current characteristics of Na-zirpsio

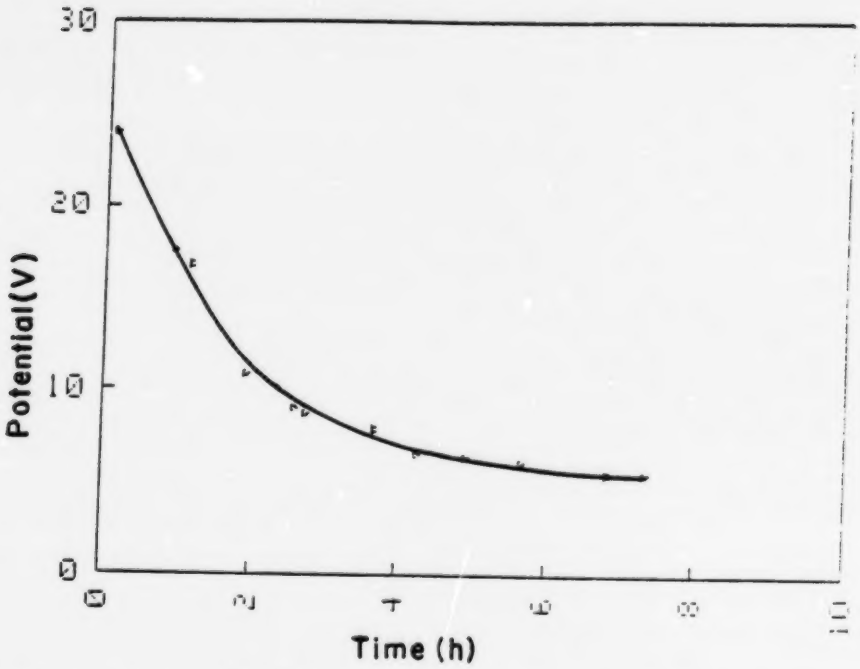

Fig. 4 - The change in field voltage during exchange at constant current at 15.0 ma

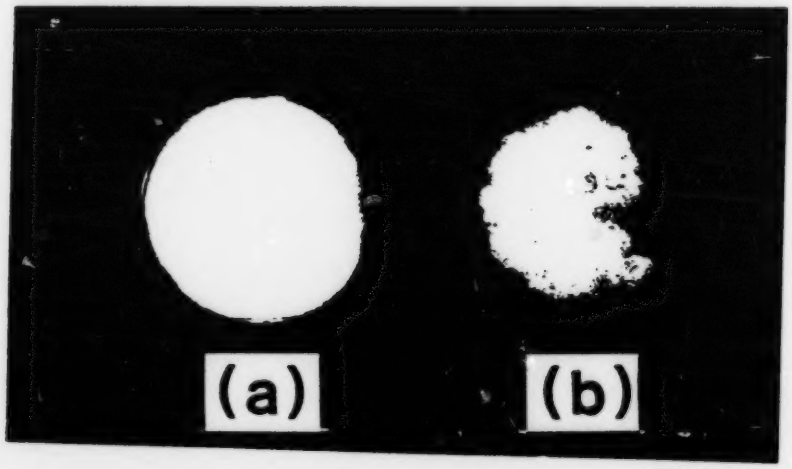

Fig. 5 - Transmitted light photographs of zirpsio disc
(a) before exchange (b) after exchange

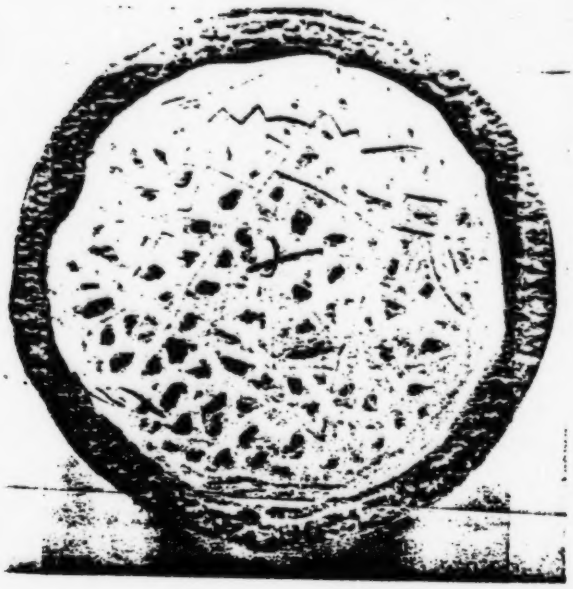

Fig. 6 - Photograph showing extensive cracking on ion exchange

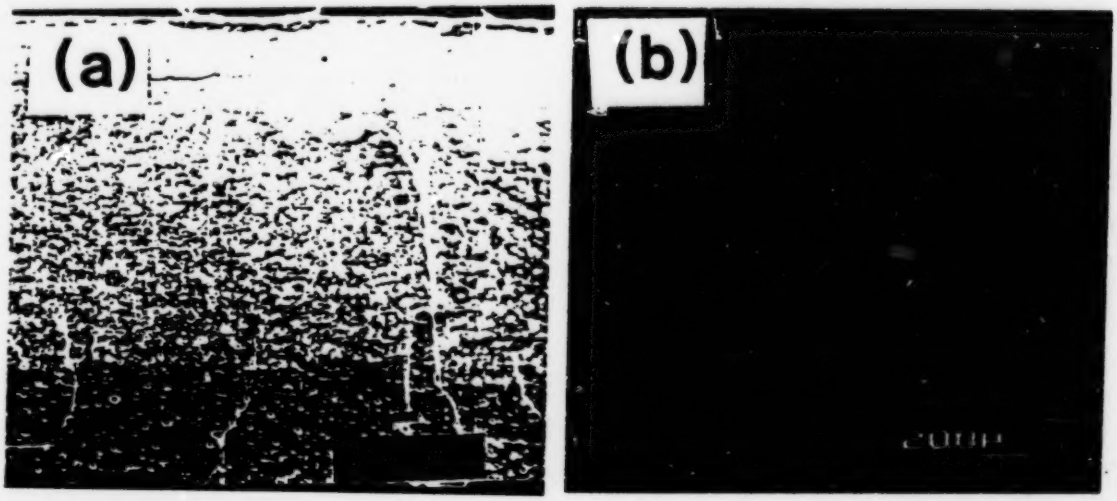

Fig. 7 - Low magnification SEM images of a partially exchanged zirpsio sample:
(a) SEM (b) Energy dispersive X-ray map of Na (K)

Fig. 8 - SEM of a cracked zone in Na-zirpsio after hydronium ion exchange

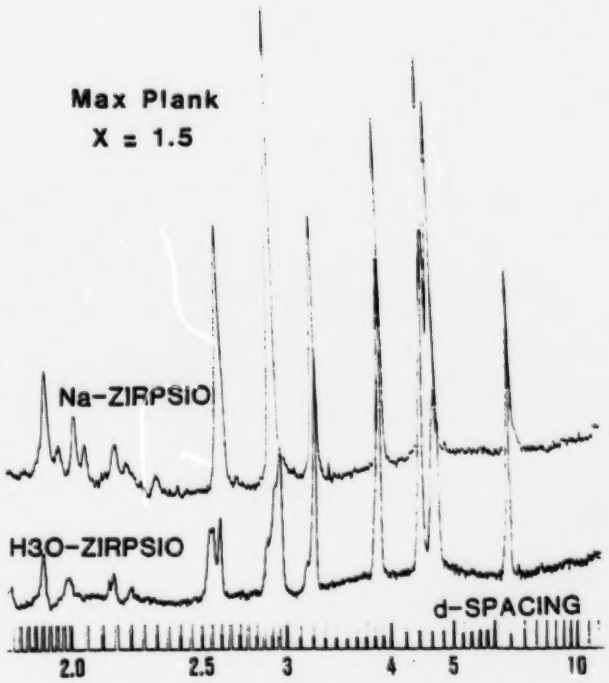

Fig. 9 - Guinier X-ray diffraction patter of Max Planck x = 1.5 Na-zirpsio and hydronium zirpsio

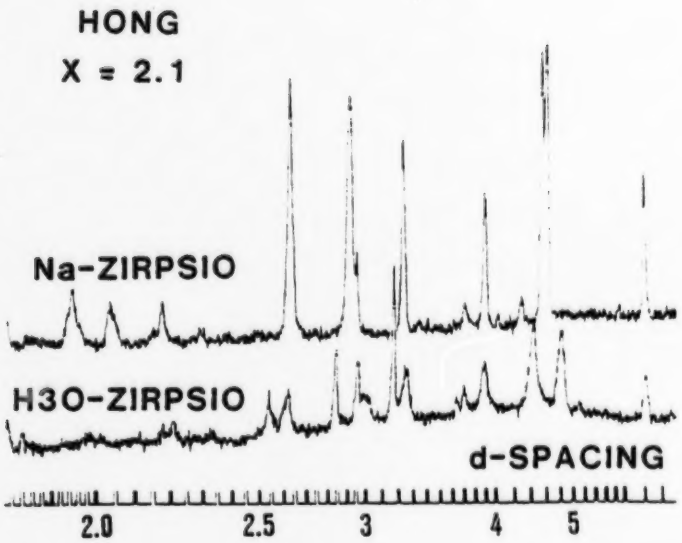

Fig. 10 - Guiner X-ray diffraction pattern of Hong x = 2.1 Na-zirpsio and hydronium zirpsio